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A. J. Nelson, K. S. Holliday, J. A. Stanford, W. K. Grant,  
R. G. Erler, P. G. Allen, W. McLean, P. Roussel

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## Adsorption of Atmospheric Gases on Pu Surfaces

A.J. Nelson<sup>1</sup>, K.S. Holliday<sup>1</sup>, J.A. Stanford<sup>1</sup>, W.K. Grant<sup>1</sup>, R.G. Erler<sup>1</sup>, P. Allen<sup>1</sup>, W. McLean<sup>1</sup> and P. Roussel<sup>2</sup>

<sup>1</sup>Lawrence Livermore National Laboratory, Livermore, CA 94550, U.S.A.

<sup>2</sup>AWE Aldermaston, Reading, Berkshire RG7 4PR, U.K.

### ABSTRACT

Surface adsorption represents a competition between collision and scattering processes that depend on surface energy, surface structure and temperature. The surface reactivity of the actinides can add additional complexity due to radiological dissociation of the gas and electronic structure. Here we elucidate the chemical bonding of gas molecules adsorbed on Pu metal and oxide surfaces. Atmospheric gas reactions were studied at 190 and 300 K using x-ray photoelectron spectroscopy. Evolution of the Pu 4f and O 1s core-level states were studied as a function of gas dose rates to generate a set of Langmuir isotherms. Results show that the initial gas dose forms Pu<sub>2</sub>O<sub>3</sub> on the Pu metal surface followed by the formation of PuO<sub>2</sub> resulting in a layered oxide structure. This work represents the first steps in determining the activation energy for adsorption of various atmospheric gases on Pu.

### INTRODUCTION

Understanding the surface dynamics of oxidation and reduction reactions on actinide materials is important to the continued development of advanced nuclear fuel technologies. Knowledge of the surface reactions with various environmental and atmospheric agents, and the subsequent degradation processes, over a wide range of temperatures are vitally important. Past reviews of the oxidation of actinide elements [1-4] illuminate the ambient reaction mechanisms and growth kinetics at atmospheric and reduced pressures.

The dynamics of gas-surface interactions depend on the energy of the gaseous species, the temperature, and the atomic structure of the solid surface. Radiological dissociation of the gaseous species and the electronic structure of actinide surfaces further enhance surface reactivity. [5] Here we investigate the chemical bonding of gas molecules adsorbed on Pu metal and oxide surfaces at 190K and 300K using X-ray photoelectron spectroscopy (XPS). The evolution of the Pu 4f and O 1s core-levels as a function of gas dose rates provides a comprehensive characterization of the oxide growth.

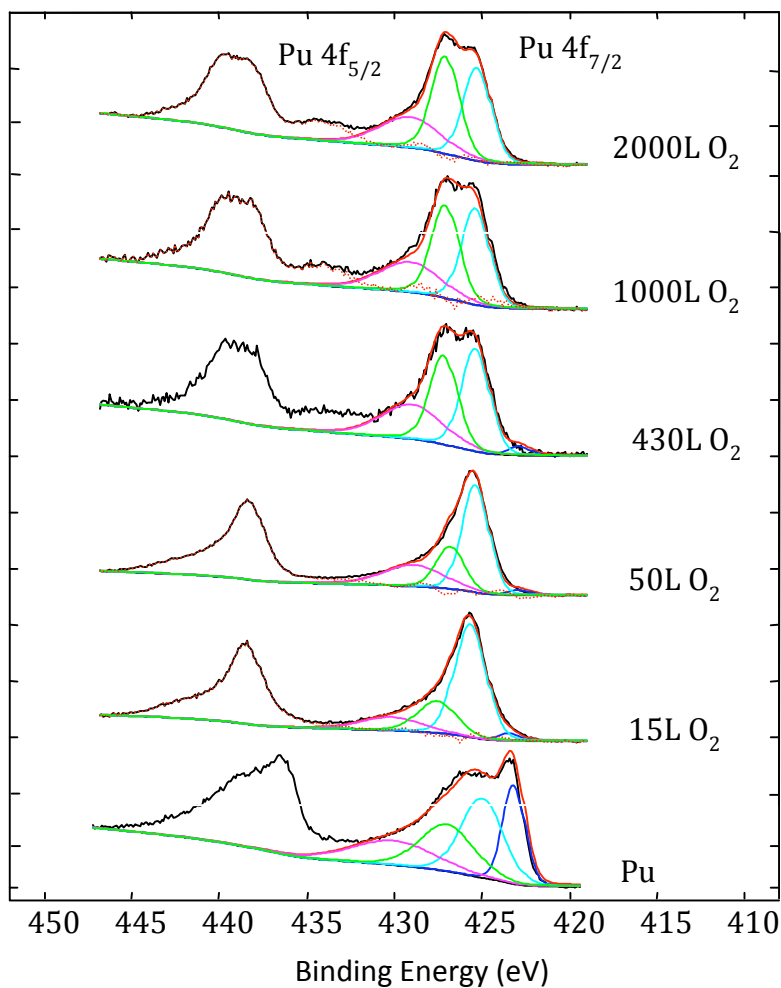
### EXPERIMENT

Gas dosing of the electropolished gallium stabilized  $\delta$ -phase Pu was performed in the UHV chamber at  $1 \times 10^{-6}$  torr after Ar-ion sputter etching to remove the native oxide. Sputter cleaning was accomplished with 4.5 kV Ar<sup>+</sup> rastered over a broad 7 x 7 mm area giving a sputter etch rate of  $\approx 0.1$  nm/min. XPS experiments were subsequently performed using a Physical Electronics 5400 system with an Al K $\alpha$  radiation (1486.6 eV) source for excitation and a hemispherical analyzer. XPS spectra were acquired in normal emission geometry. The pass

energy was 22.35 eV giving an energy resolution of 0.5 eV that when combined with the natural Al K $\alpha$  line width gives a resolvable XPS peak width of approximately 1.5 eV FWHM. Deconvolution of non-resolved peaks was accomplished using Multipak 9.2 (PHI) curve fitting routines with asymmetric line-shape for the metal and Gaussian-Lorentzian line-shape for the oxides, all with a Shirley background. The collected data were referenced to an energy scale with binding energies for Cu 2p $_{3/2}$  at 932.72 $\pm$  0.05 eV and Au 4f $_{7/2}$  at 84.01 $\pm$  0.05 eV.

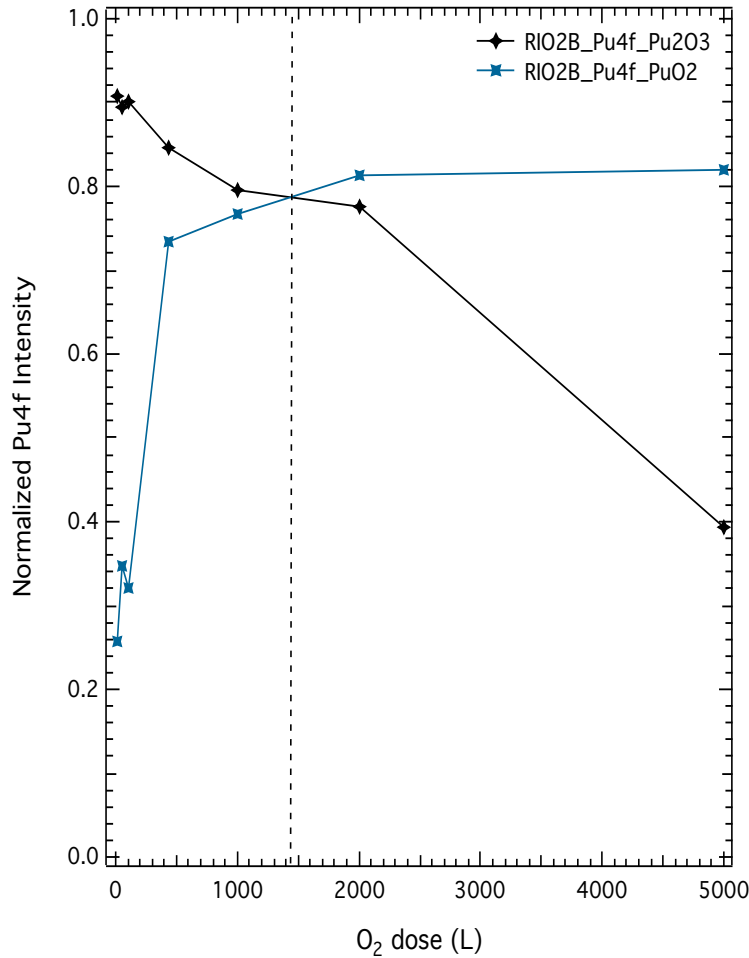
## RESULTS AND DISCUSSION

Figure 1 shows the evolution of the Pu 4f $_{7/2,5/2}$  spin-orbit pair as a function of O $_2$  dosing at a substrate temperature of 300K. The Pu 4f curve fits show three components due to Pu $^0$  (422.0 eV), Pu $^{3+}$  (424.6 eV) and Pu $^{4+}$  (426.2 eV). The area of each Pu 4f $_{7/2}$  component was normalized to the total Pu 4f $_{7/2}$  area and plotted as a function of O $_2$  dose as shown in Fig. 2. These results show that at 300K the initial gas dose forms Pu $_2$ O $_3$  on the Pu metal surface followed by the formation of PuO $_2$  resulting in a layered oxide structure. Note however that both figures show incomplete PuO $_2$  coverage of the Pu $_2$ O $_3$  on the Pu metal surface.



**Figure 1.** Select Pu 4f $_{7/2,5/2}$  spectra for O $_2$  dosing at 300K showing the Pu $^0$ , Pu $^{3+}$  and Pu $^{4+}$  Gaussian-Lorentzian components.

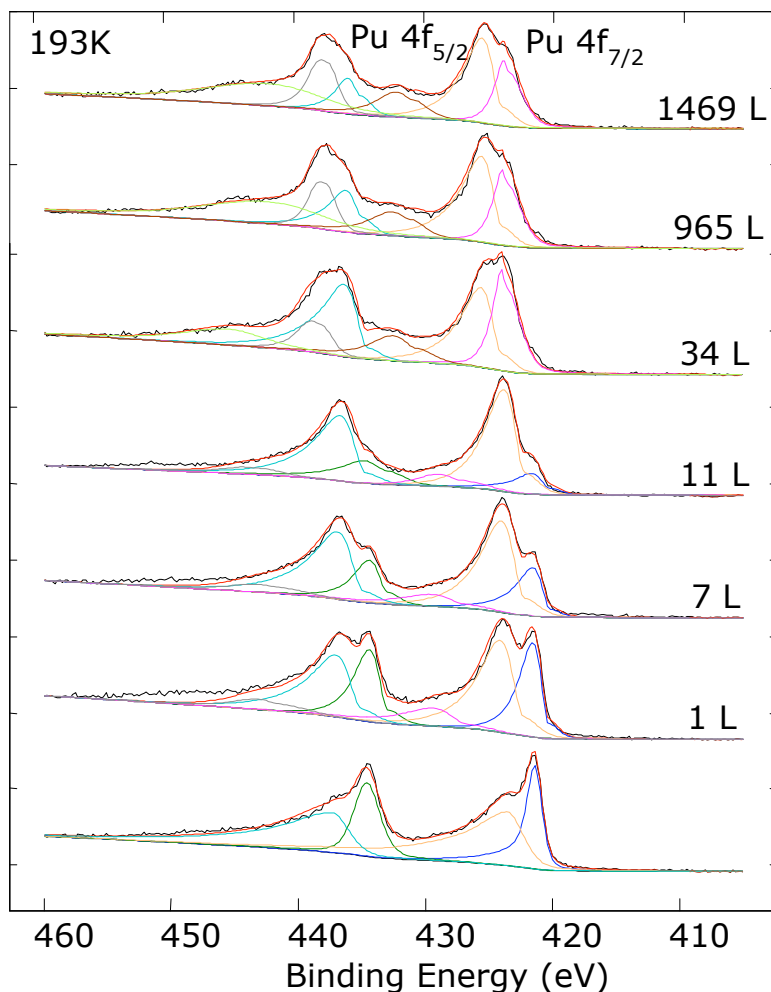
Competition between oxide growth and auto-reduction of  $\text{Pu}^{4+}$  to  $\text{Pu}^{3+}$  in vacuum was not easily overcome at ambient temperature. Cooling the Pu substrate during gas dosing was found to slow the  $\text{Pu}^{4+}$  to  $\text{Pu}^{3+}$  reduction in ultrahigh vacuum.



**Figure 2.** Pu oxide growth profile at 300K based on normalized areas of the  $\text{Pu}^0$ ,  $\text{Pu}^{3+}$  and  $\text{Pu}^{4+}$  components from Figure 1.

The evolution of the  $\text{Pu}^0$ ,  $\text{Pu}^{3+}$  and  $\text{Pu}^{4+}$  4f components as a function of  $\text{O}_2$  dosing at a substrate temperature of 193K are presented in Figure 3. Each component was again normalized to the total Pu 4f<sub>7/2</sub> area and plotted as a function of  $\text{O}_2$  dose (Fig. 4). Again we note incomplete  $\text{PuO}_2$  coverage of the  $\text{Pu}_2\text{O}_3$  on the Pu metal surface. Angle-resolved measurements did not indicate the presence of  $\text{PuO}_2$  islands leading us to invoke the Cabrera-Mott theory [6, 7] to describe the oxidation of Pu metal at these low temperatures. Typical thermal diffusion mechanisms are quenched at these lower temperatures, so Cabrera and Mott theorized that cation or anion diffusion occurs under the influence of a potential across the growing oxide film. Specifically, an electronic equilibrium exists between the gas-oxide and metal-oxide interfaces that results in field assisted diffusion of oxygen anions across these interfaces at low

temperature. [8] These initial analyses of the kinetic and equilibrium data assume surface energetic heterogeneity of the polycrystalline Pu surface.



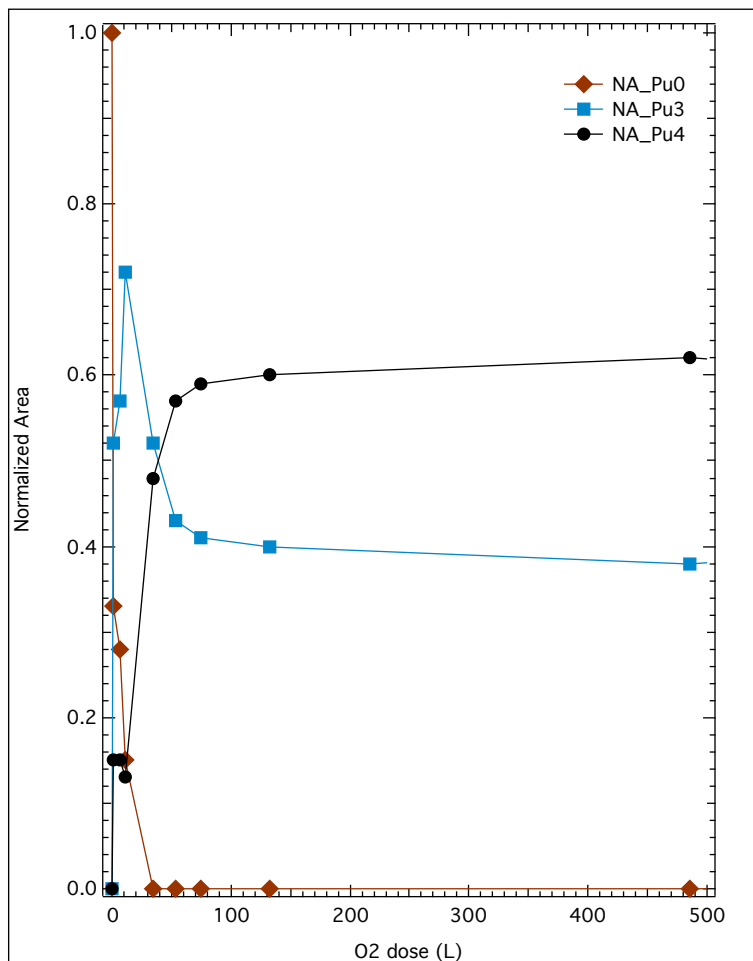
**Figure 3.** Select Pu 4f<sub>7/2,5/2</sub> spectra for O<sub>2</sub> dosing at 193K showing the evolution of the Pu<sup>0</sup>, Pu<sup>3+</sup> and Pu<sup>4+</sup> components.

## CONCLUSIONS

XPS was used to observe the growth of a PuO<sub>2</sub> / Pu<sub>2</sub>O<sub>3</sub> / Pu layered structure at 190K and 300K. The two equilibrium adsorption isotherms at 190K and 300K are the first steps in determining the activation energy for adsorption of various atmospheric gases on Pu. Further experiments are essential to determine the initial sticking probability and the kinetics of gas adsorption on actinide surfaces.

## ACKNOWLEDGMENTS

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**Figure 4.** Pu oxide growth profile at 193K based on normalized areas of the  $\text{Pu}^0$ ,  $\text{Pu}^{3+}$  and  $\text{Pu}^{4+}$  components from Figure 3.

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